

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
19 September 2002 (19.09.2002)

PCT

(10) International Publication Number
WO 02/072482 A2

- (51) International Patent Classification⁷: **C02F 1/56**
- (21) International Application Number: **PCT/EP02/02233**
- (22) International Filing Date: **1 March 2002 (01.03.2002)**
- (25) Filing Language: **English**
- (26) Publication Language: **English**
- (30) Priority Data:
0106233.0 **14 March 2001 (14.03.2001)** **GB**
- (71) Applicant (*for all designated States except US*): **CIBA SPECIALTY CHEMICALS WATER TREATMENTS LIMITED** [GB/GB]; Cleckheaton Road, Low Moor, Bradford, West Yorkshire BD12 0JZ (GB).
- (72) Inventors; and
- (75) Inventors/Applicants (*for US only*): **WEIR, Steven** [GB/GB]; 29 St. Thomas Gardens, Bradley, Huddersfield, West Yorkshire HD2 1SL (GB). **STRINGER, Mark** [GB/GB]; 15 Woodhall Croft, Pudsey, Leeds, West Yorkshire LS28 7TU (GB).
- (74) Common Representative: **CIBA SPECIALTY CHEMICALS WATER TREATMENTS LIMITED**; Cleckheaton Road, Low Moor, Bradford, West Yorkshire BD12 0JZ (GB).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: **PROCESS FOR FLOCCULATING SUSPENSIONS**

(57) Abstract: A process of flocculating and dewatering an aqueous suspension of suspended solids comprising, introducing into the suspension, (a) polymer composition of between 40% and 60% by weight and, (b) polymer composition of between 0.05 to 0.2% by weight, characterised in that the polymer compositions are introduced into the substrate substantially simultaneously. The process brings about improvements in filtration and cake solids.

WO 02/072482 A2

Process For Flocculating Suspensions

This invention relates to processes of flocculating aqueous suspensions in order to effect separation of solids from said suspension.

It is well known to apply polymeric flocculants to aqueous suspensions in order to separate solids from the suspension. For instance it is common practice to flocculate and then dewater suspensions containing either suspended solid organic material or mineral solids. For instance it is common practice to flocculate sludges such as sewage sludge, waste waters, textile industry effluents, red mud from the Bayer Alumina process and suspensions of coal tailings etc. Flocculants are also commonly used in paper-making processes by addition of polymeric flocculants to the cellulosic suspension. Flocculation is usually achieved by mixing into the suspension polymeric flocculant, allowing the suspended particles to flocculate and then dewatering the flocculated suspension. In papermaking this removal of water from the cellulosic suspension is often referred to as draining.

High molecular weight polymeric flocculants are commonly used for this purpose. High molecular weight flocculants may be cationic, anionic, nonionic or amphoteric in nature. The choice of polymeric flocculant will largely depend upon the substrate, which is being treated. For instance it is common practice to use high molecular weight cationic flocculants to treat aqueous suspensions comprising suspended organic material, for instance sewage sludge. In paper-making it is known to use either cationic, nonionic, anionic or amphoteric flocculants. Flocculation of mineral suspensions is frequently effected by use of anionic flocculants.

It is also known to use two different polymeric flocculants in the same process. The flocculants may have the same charge (co-ionic). For instance in commercial practice in the dewatering sewage sludge these may be co-ionic. In other processes it is known to apply two polymers of opposite charge

(counter-ionic). Where two polymeric flocculants are applied to an aqueous suspension they may be added to simultaneously or more usually sequentially.

It is standard practice to apply polymers as aqueous compositions to flocculate suspensions containing suspended organic material. Generally the compositions of polymers are relatively dilute, for instance below 0.5%, often below 0.3% and usually 0.1% to below 0.2% by weight.

Polymers are usually provided as a solid particulate product or as a reverse phase dispersion or emulsion. It is standard practice to dissolve the polymer into water by dispersing the polymer particles in a flowing stream of water in the case of the solid particulate product or in the case of the emulsion or dispersion, inversion into water, by use of activator surfactants. The polymer composition thus formed is frequently at a concentration above 0.3%, often in the range 0.4% to 1% and usually about 0.5%. This more concentrated composition of polymer may be too concentrated to add directly to the suspension in many instances, since received wisdom suggests that there would be inadequate distribution of the flocculant throughout the suspension and as a consequence the flocculation process would be impaired.

It is therefore common practice to first of all provide a more concentrated composition of polymer and then dilute the polymer composition prior to application. Often the diluted composition will have a concentration of below 0.2%, for instance within the range 0.05 to 0.2% by weight and frequently between 0.1 and 0.2% by weight. This dilute composition of polymer is normally metered directly into the suspension prior to the dewatering stage.

There is a desire to improve the efficiency of the flocculation processes, to either bring about an increased dewatering effect, such as higher cake solids or in the alternative achieve a constant acceptable level of dewatering efficiency but using a lower dose of flocculant. This is true in a variety of flocculation

processes, including dewatering of sewage sludge, slurries of coal tailings, red mud and in papermaking.

It would therefore be desirable to provide an improved method of flocculating and dewatering aqueous suspensions of solids, in particular to provide increased dryness of the dewatered solids for an equivalent dose of flocculant or to provide the same degree of dryness of dewatered solids but using a reduced dose of flocculant. It would also be desirable to provide a process which provides faster dewatering.

The invention relates to a process of flocculating and dewatering an aqueous suspension of suspended solids comprising, introducing into the suspension,

(a) polymer composition of between 40% and 60% by weight and,

(b) polymer composition of between 0.05 to 0.2% by weight,

characterised in that the polymer compositions are introduced into the substrate substantially simultaneously.

The compositions (a) and (b) may be metered directly into the suspension as separate compositions. By substantially simultaneously the two compositions should be added at approximately the same dosing point. Where the compositions (a) and (b) are added to the suspension separately, they may be added in either order. For instance if the composition (b) is added first the polymer (a) may be added after flocculation has commenced but should be added before the dewatering stage and before any high shear stage, such as pumping or screening stages. Alternatively, it may be desirable to add the composition (b) after the addition of the composition (a). When the compositions are added separately it may be appropriate to allow or apply some degree mixing between the dosing stages in order to allow the first polymer dose to become distributed throughout the suspension solids. This mixing may for instance include allowing the treated suspension to pass some distance along a flow line which optionally contains bends, baffles, constrictions or other features which induce gentle mixing.

Preferably the polymer compositions are introduced simultaneously.

More preferably the polymer compositions are introduced into the suspension as a reverse phase dispersion.

The polymer composition (b) desirably has a concentration of polymer of below 1.0%, preferably below 0.5% by weight. More preferably the concentration of the dilute composition is in the range 0.01 to 0.4%, most preferably around 0.2% by weight.

According to the invention the polymer dissolved in the polymer composition (b) may be either cationic, anionic or non-ionic.

The component (a) according to the invention desirably has a concentration of polymer in the range 5 to 60%. More preferably the concentration of the composition (a) is around 50% by weight.

When the polymer in either the composition (a) or (b) is cationic, said cationic polymer may be formed by polymerisation of at least one cationic monomer alone or with other monomers. Suitable cationic monomers include quaternary ammonium or acid salts of monomers which contain amine groups. Preferably the cationic polymer is formed from a monomer or blend of monomers comprising at least one cationic monomer selected from the group consisting of quaternary ammonium and acid salts of dimethylaminoethyl (meth) acrylate, quaternary ammonium and acid salts of dimethylaminoethyl (meth) acrylamide and diallyldimethyl ammonium chloride. The cationic monomers may be homopolymerised or copolymerised with other monomers, for instance acrylamide. In addition to vinyl addition polymers, the cationic polymer may include polymers obtained by condensation or addition reactions. For instance suitable cationic polymers include adducts of amines with epihalohydrins or dihaloalkanes, polyamides and polyethylene imines.

In the case where the polymer in either composition (a) or (b) is anionic, said anionic polymer may be formed by polymerisation of at least one anionic monomer alone or with other monomers. Suitable anionic monomers include ethylenically unsaturated monomers comprising carboxylic acid or sulphonic acid groups. Preferably the anionic polymer is formed from a monomer or blend of monomers comprising at least one anionic monomer selected from the group consisting of (meth) acrylic acid, 2-acrylamido-2-methylpropane sulphonic acid, alkali metal and ammonium salts thereof.

If the polymer in either composition (a) or (b) is nonionic, said anionic polymer may be formed by polymerisation of suitable non-ionic monomers, for instance acrylamide or methacrylamide.

The polymers suitable for composition (a) may be prepared by any convenient polymerisation process, for instance reverse phase suspension polymerisation, reverse phase emulsion polymerisation, composition polymerisation and the like. Thus suitable polymers may be provided in the form of reverse phase emulsions, reverse phase dispersions or aqueous compositions such as aqueous polymer dispersions.

Preferably composition (a) is a water in oil emulsion, a polymer in oil dispersion or an aqueous polymer dispersion.

The polymers suitable for the composition (b) may be prepared by any convenient polymerisation process, for instance gel polymerisation, reverse phase suspension polymerisation, reverse phase emulsion polymerisation, composition polymerisation and the like. Thus suitable polymers may be provided in the form of granulated powders, beads, reverse phase emulsions, reverse phase dispersions or aqueous compositions such as aqueous polymer dispersions.

Preferably composition (b) is an aqueous preparation of a water in oil emulsion or a polymer in oil dispersion, or an aqueous polymer dispersion or an aqueous preparation of a solid grade polymer.

The polymers according to the invention may be prepared as substantially linear polymers or as branched or structured polymers. Structured or branched polymers are usually prepared by inclusion of polyethylenically unsaturated monomers, such as methylene-bis-acrylamide into the monomer mix, for instance as given in EP-B-202780. Preferably however, the polymers are substantially linear and are prepared in the form of a bead or powdered product.

A particularly preferred group of polymers includes copolymers of acrylamide with at least one cationic monomer selected from the group consisting of quaternary ammonium and acid salts of dimethylaminoethyl (meth) acrylate, quaternary ammonium and acid salts of dimethylaminoethyl (meth) acrylamide and diallyldimethyl ammonium chloride, having an intrinsic viscosity of at least 4 dl/g. The cationic acrylamide polymers may comprise 10 to 90% by weight acrylamide and 10 to 90% by weight cationic monomer(s).

The invention is suited to a variety of processes involving flocculation and dewatering. Processes of particular relevance include dewatering sewage sludges, dewatering mineral suspensions, dewatering of paper mill sludges, dewatering of deinked cellulosic sludges e.g. from paper deinking plants and also papermaking processes.

The following examples serve to illustrate the invention.

Example 1

Reverse phase emulsion of a copolymer of acrylamide with dimethylaminoethyl acrylate, methyl chloride quaternary ammonium (80/20 weight/weight), intrinsic viscosity at least 10dl/g, is prepared at 50% concentration.

This emulsion is then diluted with an appropriate amount of water to produce aqueous preparations at 0.1 and 0.25% concentration.

500ml aliquots of Rotherham (Yorkshire, England) sewage sludge are treated with dilute polymer (0.1%) and (0.25%), concentrated polymer (50%) and using simultaneous addition (the simultaneous addition of 0.1% and 50% concentration compositions at different addition points to the sewage sludge) each at various doses of cationic polymer. The treated sludge is mixed at 1500 rpm for 15 seconds. The flocculation efficiency is measured by free drainage using a 8cm diameter sieve.

The free drainage results are shown in Table 1. The "simultaneous addition" corresponds to the simultaneous addition of 0.1% and 50% concentration compositions at different addition points to the sewage sludge.

Table 1

Polymer composition	5 second filtrate volume (ml) for each dose			
	40	60	80	100
0.1%	120	310	320	
0.25%	112	308	304	
50%	80	80	100	130
Simultaneous addition	120	345	350	345

The results clearly show the advantage of using the simultaneous addition of concentrated compositions and dilute compositions of the cationic polymer.

Example 2

Aqueous polymer dispersions of a copolymer of acrylamide with dimethylaminoethyl acrylate, methyl chloride quaternary ammonium (40/60 weight/weight), intrinsic viscosity at least 8dl/g, is prepared at 50% concentration.

This dispersion is then diluted with an appropriate amount of water to produce aqueous preparations at 0.1 and 0.25% concentration.

500ml aliquots of Rotherham (Yorkshire, England) sewage sludge are treated with dilute polymer (0.1%) and (0.25%), concentrated polymer (50%) and using simultaneous addition (the simultaneous addition of 0.1% and 50% concentration compositions at different addition points to the sewage sludge) at various doses of cationic polymer. The treated sludge is mixed at 1500 rpm for 15 seconds. The flocculation efficiency is measured by free drainage using a 8cm diameter sieve.

The free drainage results are shown in Table 2. The "simultaneous addition" corresponds to the simultaneous addition of 0.1% and 50% concentration compositions at different addition points to the sewage sludge.

Table 2

	5 second filtrate volume (ml) for each dose				
Polymer composition	50	60	70	80	90
0.1%	110	150	200	250	260
0.25%	110	140	200	240	240
50%	90	170	260	220	180
Simultaneous addition	190	230	240	200	170

The results clearly show the advantage of using simultaneous addition of concentrated compositions and dilute compositions of the cationic polymer.

Claims

1. A process of flocculating and dewatering an aqueous suspension of suspended solids comprising, introducing into the suspension,
 - (a) polymer composition of between 40% and 60% by weight and,
 - (b) polymer composition of between 0.05 to 0.2% by weight,characterised in that the polymer compositions are introduced into the substrate substantially simultaneously.
2. A process according to claim 1 in which the composition (a) is a water in oil emulsion, a polymer in oil dispersion or an aqueous polymer dispersion.
3. A process according to claim 1 in which the composition (b) is an aqueous preparation of a water in oil emulsion or a polymer in oil dispersion, or an aqueous polymer dispersion or an aqueous preparation of a solid grade polymer.
4. A process according to any one of claims 1 to 3 in which the polymer composition (b) comprises a cationic polymer, an anionic polymer or a nonionic polymer.
5. A process according to any one of claims 1 to 4 in which the composition (a) comprises a cationic polymer, an anionic polymer or a nonionic polymer.
6. A process according to any one of claims 1 to 5 in which polymer(s) in either the composition (a) or (b) is cationic and has been formed from a monomer or blend of monomers comprising at least one cationic monomer selected from the group consisting of quaternary ammonium and acid salts of dimethylaminoethyl (meth) acrylate, quaternary ammonium and acid salts of dimethylaminoethyl (meth) acrylamide and diallyldimethyl ammonium chloride.

7. A process according to any one of claims 1 to 6 in which polymer(s) in either the composition (a) or (b) is anionic and has been formed from a monomer or blend of monomers comprising at least one anionic monomer selected from the group consisting of (meth) acrylic acid, 2-acrylamido-2-methylpropane sulphonic acid, alkali metal and ammonium salts thereof.
8. A process according to any one of claims 1 to 7 in which polymer(s) in either the composition (a) or (b) is nonionic and has been formed from acrylamide or methacrylamide.
9. A process according to any one of claims 1 to 8 in which the cationic polymer of the compositions (a) or (b) is a copolymer of acrylamide and at least one cationic monomer selected from the group consisting of quaternary ammonium and acid salts of dimethylaminoethyl (meth) acrylate, quaternary ammonium and acid salts of dimethylaminoethyl (meth) acrylamide and diallyldimethyl ammonium chloride, having an intrinsic viscosity of at least 4 dl/g.
- 10 A process according to any one of claims 1 to 9 in which the dewatering process is selected from the group consisting of dewatering sewage sludge, dewatering a mineral suspension, dewatering a paper mill sludge, dewatering a deinked cellulosic sludge and a papermaking process.